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METHOD FOR PREPARATION OF NEW TRISAZO DYES

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The invention concerns a method for preparation of new trisazo dyes of general formula 1, in which A denotes a nitrophenyl group or its derivative and B denotes a hydroxyphenyl or methylhydroxyphenyl group, or an acetylacetic arylide group or a heterocyclic group. These dyes color fibers of plant origin, leather and paper to different shades of green.

By the method according to the invention, a compound of formula 2 is coupled in an acid medium with diazotized nitroaniline or its derivative, whereupon the obtained compound of general formula 3, in which A has the aforementioned meaning, is coupled with phenol, cresol, acetylacetic arylide or a heterocyclic compound.

Coupling of the compound of formula 2 with diazotized nitroaniline or its derivative is carried out by using a hypostoichiometric amount of the active component or a stoichiometric amount or a slight excess. When a stoichiometric amount or excess of active component is used in the reaction medium, an insignificant amount of diazonium compound remains, which exerts, during its presence in this medium, an unfavorable effect on the subsequent process, as a result

of formation by this compound of insoluble dyes during further synthesis. The reaction mass must be left in this situation until decomposition of the above-mentioned excess diazonium compound or a solution of 1-amino-8-naphthol-3,6-disulfonic acid [can be] added to it, which forms a violet dye with the excess diazonium compound, which leaves, together with the waste, in the final phase of the process during filtration.

The dyeing obtained with the new dyes prepared by the method according to the invention is characterized by good lightfastness and resistance to wet environments.

The method according to the invention is illustrated without limiting its scope by the following examples, in which parts and percents denote parts and percents by weight, and the temperatures are stated in degrees Celsius.

Example I. 18.5 parts 4,4'-diaminostilbene-2,2'-disulfonic acid and 4 parts NaOH are added to a mixture of 200 parts water and 55 parts ice. The obtained solution is treated with 35 parts 30% hydrochloric acid, whereupon a solution of 7 parts sodium nitrite in 17 parts water is added to the formed suspension over 30 min and the entirety mixed for 1 h. A solution obtained by dissolving 17.6 parts 1-naphthyl-8-amino-3,6-disulfonic acid in 300 parts water with addition of 4.5 parts sodium carbonate is added over 50 min to the obtained suspension of 4,4'-tetraazostilbene-2,2'-disulfonic acid. The reaction mixture is agitated for 12 h, keeping the pH between 2 and 3 by gradual dropwise addition during the reaction of a sodium acetate solution obtained by dissolving 10.7 parts acetate in 130 parts water. On completion of the coupling reaction, a compound of formula 2 is obtained, which is left in the reaction mixture for further coupling.

6.9 parts p-nitroaniline in a mixture of 100 parts water and 17 parts 30% hydrochloric acid are simultaneously added with addition of ice to obtain a temperature of 0-2°C for the diazotization reaction by addition of 3.9 parts sodium nitrite dissolved in 10 parts water, all at once, whereupon the entirety is mixed for 2 h at a temperature of 0-2°C.

The obtained mass containing the diazonium compound of p-nitroaniline is introduced into the reaction mixture obtained by the method just described, containing the compound of formula 2, whereupon a solution of 12.4 parts sodium carbonate dissolved in 50 parts water is added to the formed mixture to obtain a pH of 5-6. The entirety is mixed for 3 h to complete decomposition of the excess diazonium compound of p-nitroaniline unconsumed during the coupling reaction. A compound of general formula 3 is obtained, in which A denotes a 4-nitrophenyl group.

The mass, after the synthesis reaction of the compound of formula 3, is introduced into a mixture of 4.7 parts phenol, 150 parts water and 2 parts sodium hydroxide, then cooled to a temperature of 10-15°C. The entirety is mixed for 10 h, whereupon the isolated dye is filtered. After drying, 55 parts of a trisazo dye of general formula 1 are obtained, in which A denotes a

4-nitrophenyl group and B denotes a 4-hydroxyphenyl group, which dyes green the fibers of plant origin, leather and paper.

Example II. The procedure of Example I is followed, using 5.4 parts m-cresol instead of phenol. 60 parts of a dye of general formula 1 are obtained, in which A denotes a 4-nitrophenyl group and B denotes a 2-methyl-4-hydroxyl group, which dyes green the fibers of plant origin, leather and paper.

Example III. The procedure of Example I is followed, using m-nitroaniline instead of p-nitroaniline, and 8.4 parts acetylacetic anilide instead of phenol. 62 parts of a dye with general formula 1 are obtained, in which A denotes a 3-nitrophenyl group, and B denotes an acetyl acidic anilide group, which dyes green the fibers of plant origin, leather and paper.

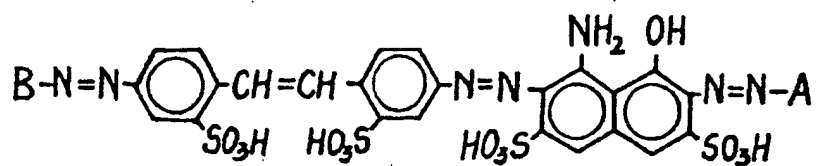
Example IV. The procedure of Example I is followed, using 8.7 parts 2-chloro-4-nitroaniline instead of p-nitroaniline, and 12.7 parts of 1-(4-sulfophenyl)-3-methylpyrazol-5-one, instead of phenol in 150 parts water with addition of 12.7 parts sodium carbonate. 65 parts of a dye of general formula 1 are obtained, in which A denotes a 2-chloro-4-nitrophenyl group and B denotes a 1-(4-sulfophenyl)-3-methylpyrazol-5-one [sic; ...phenyl)-3-methylpyrazol-5-one] group, which dyes green the fibers of plant origin, leather and paper.

Example V. The procedure of Example I is followed, in which the unreacted excess of active component during the coupling reaction of the compound of formula 2 with diazotized p-nitroaniline is decomposed by addition to the reaction mass after a half-hour of mixing of a solution of 1-naphtho-8-amino-3,6-disulfonic acid in water with addition of sodium carbonate, to complete coupling with the remaining excess p-nitroaniline. 54 parts of a dye of general formula 1 are obtained, in which the symbols have the meaning defined in Example I.

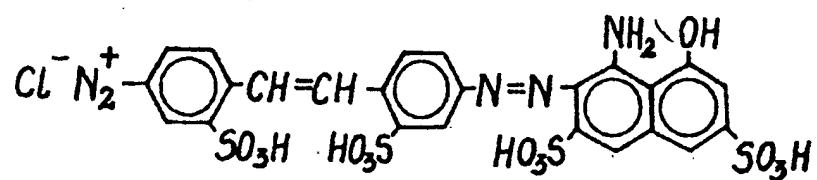
Example VI. The procedure of Example I is followed, in which a hypostoichiometric amount of p-nitroaniline is used in an amount of 6.55 parts of this compound in a mixture with 100 parts water and 16 parts 30% hydrochloric acid, and diazotization of the above-mentioned compound is run, using 3.7 parts nitrite in 10 parts water. The reaction mass during coupling of the compound of formula 2 with p-nitroaniline is mixed for 0.5 h. 55 parts of a dye of general formula 1 are obtained, in which the symbols have the meanings defined in Example I.

Claim

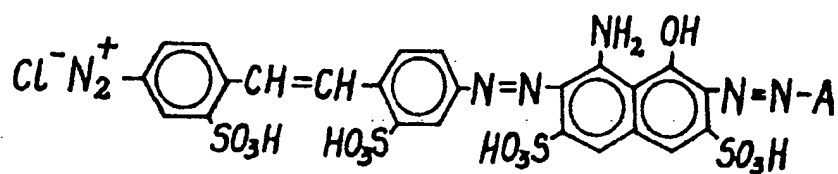
Method for production of new trisazo dyes of general formula 1, in which A denotes a nitrophenyl group or its derivative, and B denotes an acetylacetic arylide group or a heterocyclic group, characterized by the fact that the compound of formula 2 is coupled in an acid medium with diazotized nitroaniline or its derivative, whereupon the obtained compound of general formula 3, in which A has the aforementioned meaning, is coupled with phenol, cresol, acetylacetic arylide or a heterocyclic compound.



Formula 1



Formula 2



Formula 3